PREPARATION AND CHARACTERIZATION OF FORMALDEHYDE FREE WOOD ADHESIVES LIGNIN EXTRACTED FROM OIL PALM EMPTY FRUIT BUNCH

by

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Praise is due to Allah Whose worth cannot be described by speakers, Whose bounties cannot be counted by calculators and whose claim (to obedience) cannot be satisfied by those who attempt to do so, Whom the height of intellectual courage cannot appreciate, and the divings of understanding cannot reach; He for whose description no limit has been laid down, no eulogy exists, no time is ordained and no duration is fixed. First of all, the best thanks and praise to Allah almighty, who helped me and make it easy for me to reach this goal. First and foremost, I would like to express my deepest gratitude and sincere thanks goes to my supervisor, Assoc. Prof. Afidah Abdul Rahim and Assoc. Prof. Mohamad Nasir Mohamad for giving me an opportunity to work in their laboratory during my study and giving me their invaluable guidance, continuous encouragement and generous support throughout this work. I would like to express my deepest gratitude to the government of Iraq, the government of Malaysia, Materials Research Directorate, Ministry of Science and Technology, Iraq, and Universiti Sains Malaysia for the financial and technical supports. My grateful acknowledgement to Universiti Sains Malaysia of funding this research project under RU grants 1001/PKIMIA/854002. I would also like to thank all staff members of Institute of Postgraduate Studies (IPS), the School of Chemical Sciences, School of Physics and School of Biological Sciences-USM for their help and for the use of necessary equipments. I wish to express my warm and sincere thanks to all my best colleagues and friends. Thank you Dr. Adel Mostafa Kamel for his encouragement. My heartfelt gratitude towards my family: particularly my loving wife, my daughters (Manar, Aya, Yamam), my brothers and my sisters, for their continuous love, prayer, support and patience throughout my PhD study. Thank you all.

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LIST OF ABBREVIATIONS

AEL	Autocatalyzed ethanol lignin
ASAM	Alkaline Sulfite Anthraquinone Methanol
BT	Bentonite
BWT	Boiling water test
CEC	Cation exchange capacity
CPF	Commercial phenol formaldehyde
DBE	Double bond equivalent
DMSO-d_6	Deuterated dimethyl sulfoxide
DSC	Differential scanning calorimeter
DSP	Degraded soybean-protein
DTG	Derivative thermogravimetry
EFB	Empty fruit bunch
EDX	Energy dispersive X-ray spectroscopy
EHL	Enzymatic hydrolysis lignin
EIS	Electrochemical impedance spectroscopy
ER	Ethanol residue
FTIR	Fourier Transform Infrared
G	Guaiacyl
GLY	Glycerol
GPC	gel permeation chromatography
HBPs	hyperbranched polymers
HBPAE	hyperbranched poly (amine-esters)
Hexamine	Hexamethylenetetramine

KL	Kraft lignin
LPF	Lignin-phenol formaldehyde resin
MAP	Marine adhesive proteins
MF	Melamine formaldehyde resin
MMT	Montmorillonite
MTGKL	Modified tannin glyoxalated Kraft lignin
MOE	Modulus of elasticity
MOR	Modulus of rupture
MPB	Mountain pine beetle
NMR	Nuclear Magnetic Resonance
ODA	Octadecylamine
ODA-BT	Octadecylamine bentonite
OPEFB	Oil palm empty fruit bunch
OSB	Oriented strand boards
PEG	Polyethylene glycol
PEI	Polyethylenimine
PF	Phenol formaldehyde resin
PLS	Polymer/layered silicate
pMDI	4,4'-diphenylmethane diisocyanate
PO	Propylene oxide
PPO	Polypropylene oxide
*p*TSA	Para-toluene sulfonic acid
Rp	Polarization resistance
S	Syringyl
SEM	Scanning electron microscope

SSL	Spent sulfite liquor
TGA	Thermogravimetric analysis
TGKL	Tannin glyoxalated Kraft lignin
TGLP	Tannin glyoxalated lignin polyols
TGLW	Tannin glyoxalated liquefied wood
UF	urea formaldehyde resin
VOC	Volatile organic chemic
WSAD	Water-soaking-and-drying
XRD	X-ray diffraction

LIST OF SYMBOLS

d	Basal spacing
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_w/M_n	Polydispersity
Tg	glass transition temperatures
T_{max}	Maximum degradation temperature
T_{onet}	Onset temperature
Wt%	Weight percentage
θ	Diffraction angle
λ	Wavenumber

LIST OF APPENDICES

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PUBLICATIONS

1. **Abbas Hasan Faris**, Afidah Abdul Rahim, Mohamad Nasir Mohamad Ibrahim. Preparation of lignopolyols by chemical modification of Kraft lignin from oil palm lignocellulosic waste. ***Advanced Materials Research***, Vol. 1107 (2015) pp 137-141.

CONFERENCES

1. **Abbas Hasan Faris**, Afidah Abdul Rahim, Mohamad Nasir Mohamad Ibrahim. Poster, preparation of biobased-free formaldehyde wood adhesive from lignin-tannin. The proceeding of **Joint Seminar for USM-Nagaoka University of Technology Research Collaboration**, 21-22th Oct, 2013, Penang, Malaysia, p2
2. **Abbas Hasan Faris**, Afidah Abdul Rahim, Mohamad Nasir Mohamad Ibrahim. Modification of Kraft lignin extracted from oil palm lignocellulosic west by propylene oxide. The proceeding of **Regional Conference on Sold State Science and Technology (RCSSST27)**, 20-22th Dec, 2013, Sabah, Malaysia, p 71
3. **Abbas Hasan Faris**, Afidah Abdul Rahim, Mohamad Nasir Mohamad Ibrahim. Synthesis and Characterization of Kraft Lignin Based Environmentally Friendly Wood Adhesives. The proceeding of International Sciences, Technology and Engineering Conference (ISTEC), 19-21th Sep, 2014, Langkawi, Malaysia.

PENYEDIAAN DAN PENCIRIAN PEREKAT BEBAS FORMALDEHID DARIPADA LIGNIN YANG DIEKSTRAK DARIPADA TANDAN KOSONG KELAPA SAWIT

ABSTRAK

penyelidikan ini, lignin/tanin mesra alam dan cecair perekat berasaskan kayu-OPEFB telah dikaji dengan untuk menyediakan perekat kayu bebas formaldehid dan untuk meningkatkan komposisi bahan-bahan mesra alam yang boleh diperbaharui dalam formulasi pelekat kayu. buah tandan kosong kelapa sawit (OPEFB) telah digunakan sebagai bahan mentah dalam. Proses delignifikasi OPEFB telah dijalankan menggunakan pulpa Kraft dan pulpa auto-bermangkinkan etanol-air (organosolv). Poliol lignin telah disediakan daripada pencairan Kraft lignin dan daripada pencairan langsung sisa lignoselulosa OPEFB. Analisis Mannich menggambarkan bahawa lignin Kraft mempunyai jumlah kedudukan gelang aromatik aktif yang agak tinggi (2.99%) berbanding lignin organosolv (2.06%), yang menunjukkan reaksi yang menggalakkan dengan glioksal daripada lignin organosolv. Berat molekul purata produk cecair mempamerkan peningkatan yang signifikan dengan proses pencairan lignin (16427 g mol^{-1}) dan dengan proses pencairan langsung OPEFB (12203 g mol^{-1}) berbanding dengan Kraft lignin (1564 g mol^{-1}). Ciri-ciri ini mengesahkan kejayaan penyediaan produk lignin poliol yang disasarkan. Pengubahsuaian tanin menggunakan poli berantai (amina-ester) telah dikaji. Spektrum FTIR, ^{1}H NMR dan ^{13}C NMR mengsahkan kejayaan penyediaan poli (amina-ester) dan perekat tanin diubahsuai/terglioksal lignnin (MTGKL). Spesimen papan lapis dengan resin MTGKL mempamerkan sifat tahan air apabila direndam di dalam air paip selama 24 jam, tanpa pengelupasan dalam mana-mana spesimen

manakala pengelupasan terjadi bagi spesimen resin papan lapis TGKL adalah jelas. Perekat berasaskan kayu lignin juga dinilai dalam air mendidih selepas pengubahsuaian perekat poliol lignin/tanin (TGLP) dengan poliethilemina (PEI). Pada 10% PEI dengan resin TGLP, kekuatan tegangan, pengelupasan spesimen papan lapis tidak berlaku apabila didedahkan di dalam air paip dan air mendidih. Dalam konteks yang sama, kerja-kerja ini menunjukkan kemungkinan mensintesis perekat kayu tahan air dari pencairan OPEFB dengan kehadiran glioksal sebagai ejen pengawetan telah memenuhi keperluan piawaian antarabangsa yang relevan bagi pembuatan papan lapis. Spektrum FTIR mengesahkan tindak balas antara OPEFB cecair dan glioksal melalui kehadiran kumpulan C-C, C-O-C, C=O dalam struktur resol tersebat. Ujian kekuatan OPEFB jelas menunjukkan bahawa kekuatan tegangan bagi kedua-dua spesimen TGLW papan lapis kering dan basah (21.4, 19.71 MPa) masing-masing, melebihi keperluan piawaian antarabangsa yang berkaitan. Kesan daripada tanah liat tak organik dan organik pada kayu perekat terglioksal lignin poliol/tanin juga dikaji. Pencirian FTIR, XRD dan SEM menunjukkan bahawa pengubahsuaian bentonit melalui penggunaan garam oktadekilamina (ODA) telah berlaku. Kekuatan tegangan spesimen resin papan lapis TGLP meningkat dengan ketara melalui kandungan rendah ODA-BT (1. 2, dan 3% berat). Perbandingan antara resin TGLP tulen dengan komposit menunjukkan bahawa kestabilan haba telah berkurangan.

PREPARATION AND CHARACTERIZATION OF FORMALDEHYDE FREE WOOD ADHESIVES LIGNIN EXTRACTED FROM OIL PALM EMPTY FRUIT BUNCH

ABSTRACT

In this work, environment-friendly lignin/tannin and liquefied OPEFB-based wood adhesives have been studied to prepare formaldehyde-free wood adhesives and to increase the proportion of renewable environmentally friendly materials in these wood adhesive formulations. The oil palm empty fruit bunch (OPEFB) was used as raw material. The delignification processes from OPEFB were conducted using Kraft pulping and auto-catalyzed ethanol–water (organosolv) pulping. Lignin polyols were prepared from the liquefaction of Kraft lignin and from the direct liquefaction of OPEFB lignocellulosic waste. The Mannich reactivity analysis illustrated that the Kraft lignin has comparatively higher amounts (2.99%) of activated free aromatic ring positions compared with organosolv lignin (2.06%), suggesting favourable reaction with the glyoxal than organosolv lignin. The average molecular weight of liquefied product exhibited significant increase with lignin liquefaction process (16427 g mol^{-1}) and with the direct liquefaction process of OPEFB (12203 g mol^{-1}) compared with Kraft lignin (1564 $gmol^{-1}$), which confirms the successful preparation of targeted lignin polyol products. Modification of tannin using hyperbranched poly (amine-ester) has been studied. FTIR, ^{1}H NMR and ^{13}C NMR spectra confirmed the successful preparation of hyperbranched poly (amine-ester) and modified tannin/glyoxalated lignin adhesive (MTGKL). The plywood specimens with MTGKL resin exhibited water resistant properties when soaked in tap water for 24 hours, where no delamination occurred in any of the specimens while delamination

of TGKL plywood resin specimen was evident. The lignin based-wood adhesives was also evaluated in boiling water after the modification of lignin polyols/tannin adhesive (TGLP) with polyethyleneimine (PEI). At 10% of PEI with TGLP resin, the delamination of plywood specimens did not occur after exposure in the tap water and boiling water. In the same context, this work demonstrates the possibility of synthesizing water resistant wood adhesives from the liquefaction of OPEFB in the presence of glyoxal as a curing agent that meets the requirements of relevant international standards for the manufacture of plywood. The FTIR spectra confirmed the reaction between liquefied OPEFB and glyoxal through the presence of C-C, C-O-C, and C=O groups in the resol structure. Tensile strength tests clearly demonstrated that the tensile strengths for both dry and wet TGLW plywood specimens (21.4 and 19.71 MPa) respectively, surpassed the requirements of relevant international standards. The effect of inorganic and organic clay on the glyoxalated lignin polyol/tannin wood adhesive was also studied. The FTIR, XRD, and SEM characterizations indicated that the modification of bentonite via octadecylamine (ODA) salt occurred. The tensile strengths of TGLP plywood resin specimen increased significantly through the incorporation of low contents of ODA-BT (1, 2, and 3 wt%). Comparison between pure TGLP resin and the composites shows that the thermal stability was decreased.

CHAPTER 1

INTRODUCTION

1.1 General

Wood adhesives have a very important function in the industrial production of wood-based panels. The final performance of wood panels significantly depends on the efficiency of the adhesive. Thus, the success and the evolution of the modern wood panels industry have been largely attributed to the evolution of quality wood adhesives. However, the wood-based panel industry and the adhesive industry both have a high affinity towards creativity.

The use of wood adhesives has a long tradition (Keimel, 2003), with a recorded history that spans at least 3,000 years from the time of the Egyptians (River, 1994; Skeist and Miron, 1990). The evolution of industrial wood adhesives can be explained in two stages. The first stage includes the commonly used adhesives based on natural polymers such as protein, starch, soybean, etc. The main features of this type are its ease of handling and environment friendly properties, but these types of adhesives do not meet the fundamental required bonding strength and water resistance (Charles, 2005; Pizzi and Mittal, 2003). For example, casein glues were widely used in World War I to create the wood-based mainframes of aircrafts. These adhesives lacked water resistance and could be attacked by fungi and microorganisms (mold growth) (Lambuth, 2003; Scields, 1984). Their poor durability limited their use to interior applications (Conner, 2001; Lambuth, 2003; Scields, 1984). In the second stage, condensation resins based on formaldehyde have replaced natural resins; these include urea formaldehyde (UF), phenol formaldehyde (PF), and melamine formaldehyde (MF) resins that usually have better strengths and

water resistances. Condensation resins based on formaldehyde now accounts for the largest volume of wood adhesives. PF resins are highly resistant to the hydrolysis of the C-C bond between the aromatic ring and the methylene bridge. Consequently, these resins are used in moisture- and weather-resistant wood adhesives and boards, such as waterproof plywood, particleboards, and OSBs for use in exterior weather conditions (Charles, 2005; Pizzi and Mittal, 2003).

Synthetic resins derived from fossil fuels will be exhausted and may eventually contribute to CO_2 emissions, thereby influencing climate changes. These materials are non-renewable and toxic. Recent health and environmental concerns include the emission of carcinogenic volatile formaldehyde compounds, as well as the continuous fluctuation of price of oil and its derivatives. Consequently, several studies have been conducted for the development of renewable and inexhaustible natural resources for the reduction or replacement of synthetic adhesives for wood panels, thereby decreasing the emission of formaldehyde (Mozaffar et al., 2004; Nihat and Nilgül, 2002; Pizzi, 1977; Thompson, 1991; Yoosup et al., 2008).

Adhesives based on renewable resources have long been sought. However, their industrial application and large-scale production are still below the level of expectation. The obvious advantages to the use of natural biomaterials are availability, biodegradability, and lower toxicity.

1.2 Biomass

Biomass refers to all animate organic materials, including crops, marine products, and forestry residues (such as tree stumps, branches, and dead trees), as well as some organic wastes such as agricultural waste and municipal solid waste

(Demirbas and Arin, 2002; Demirbas, 2000). Therefore, a biomass resource includes plant or animal matter, which can be converted into industrial chemicals such as BTX (benzene, toluene and xylene) and polyurethane. Different kinds of plants can be cultivated for biomass, such as hemp, willow, corn, and bamboo, including different tree species such as eucalyptus and oil palm.

Biomass is a promising source of energy that can replace fossil oil. Thus, this material is important in sustainable production because it is renewable and abundant resource on Earth. The annual production of renewable materials is approximately 20×10^{10} tons. Only 3% of known renewable materials are used for non-food manufacturing, such as in the pulp and paper industry (Zhang, 2008). Biomass resources are considered to be cheaper than other resources, such as crude oil and natural gas (Zhang, 2008). In addition, the cultivation of plants and the process of burning fuel allows biomass production to have a short cycle. Plant biomass mainly consists of cellulose ($[C_6(H_2O)_5]_n$), hemicellulose ($[C_5(H_2O)_4]_n$), and lignin ($[C_{10}H_{12}O_3]_n$), with small amounts of pectin, protein, extractives, and ash, as shown in Figure 1.1. Plant biomass is also called lignocellulosic biomass (Pan, 2011).

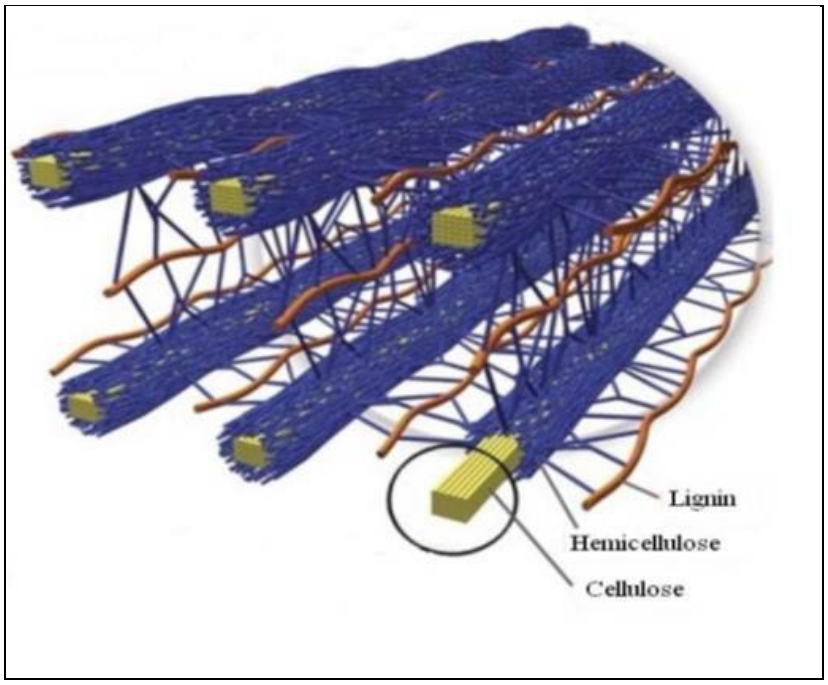


Figure 1.1: Cellulose strands surrounded by hemicellulose and lignin (Doherty et al., 2011)

The available lignocellulosic biomass has several possible applications as raw materials for energy projects, as well as for the chemical industry. Moreover, sustainability requirements and reduced CO_2 gas emissions into the atmosphere are important factors when using biomass resources.

Industrial chemicals can be obtained through the thermal depolymerization and decomposition of biomass components, such as cellulose, hemicelluloses, and lignin, in various forms of charcoal, namely, liquid, gas, and solid remnants. The potential chemicals that can be extracted from lignin conversions include methanol, ethanol, mixed alcohols, and hydrocarbons, as well as the byproduct C_1 to C_4 gases, phenol, substituted phenols, guaiacols, syringols, syringaldehyde, substituted lignins, mixed aromatic polyols, and other chemicals. To date, the wood composite production mainly depends on the petrochemicals derived from fossil oil and condensation of resin-based formaldehydes such as PF and UF resins (Liu & Li 2007).

Environmental concerns have been raised regarding the volatile organic compounds and toxic chemicals in many adhesives, as well as the continuous fluctuations in the prices of oil and its derivatives. Thus, several studies were conducted for the production of environment friendly products from biomass polymers, with a primary focus on lignin derivatives for the production of polymeric compounds, especially phenolic and epoxy resins (Methacanon, 2010; Silva et al., 2009).

Malaysia has more than 4 million hectares of oil palm plantations that yield an estimated amount of 90 million tons of renewable biomass (fronds, trunks, palm press fibers, shells, and empty fruit bunches) generated from the mechanical processes of palm oil production (Malaysia Palm Oil Board, 2013). Unfortunately, oil palm biomass is still treated as a waste, without considering the value of materials such as cellulose, hemicelluloses, and lignin (Mohamad Ibrahim et al., 2006).

Figure 1.2: View of EFB wastes piled up in a palm oil mill premise (Geng, 2013)

The remnants of biomass must be eliminated in a systematic and scientific manner because the presence of such residues is dangerous to the environment. An important element extracted from EFBs is lignin (Mohamad Ibrahim et al., 2008).

1.3 Lignin

Lignin is derived from the Latin term Lignum, which means wood (Sarkanen and Ludwig, 1971). Payen in 1838 first reported the composite nature of wood (McCarthy and Islam, 1999) and referred to the carbon-rich substance as the "encrusting material", which is an integral part of cellulose in wood. Schulze (1865) later explained that this encrusting material is lignin. Lignin is a complex phenolic polymer that is present in plant tissues. This most abundant and important natural polymer on earth second to cellulose is a byproduct of the pulp and paper industry (Methacanon, 2010; Silva et al., 2009).

Lignin exists in all vascular plants and represents approximately 15 to 30% of the dry mass of wood. Lignin is covalently associated with hemicellulose in plant cell walls. Thus, lignin is crosslinked with a variety of plant polysaccharides. Lignin is characterized by its relatively high strength, rigidity, impact strength, and resistance to ultra-violet light; lignin in wood has a high degree of heterogeneity and lacks a defined primary structure (Belanger et al., 2010). Lignins are natural phenolic materials that are well known for their role in woody biomass to provide resistance to biological and chemical decomposition.

Plant lignins can be generally divided into three classes: hardwood (angiosperm), softwood (gymnosperm), and grass (graminaceous) lignin (Pearl, 1967). Lignin is the most complex of the natural phenolic polymers (Fig. 1.3) and is

described as an amorphous three-dimensional network. The repeated units in the formation of this complex polymer are phenylpropanoid monomers, namely, the coniferyl, sinapyl, and *p*-coumaryl alcohols (Hatakeyama et al., 2002; Koullas et al., 2006; Silva et al., 2009; Zakzeski et al., 2010)**.** The phenylpropane unit of lignin is depicted in Figure 1.4.

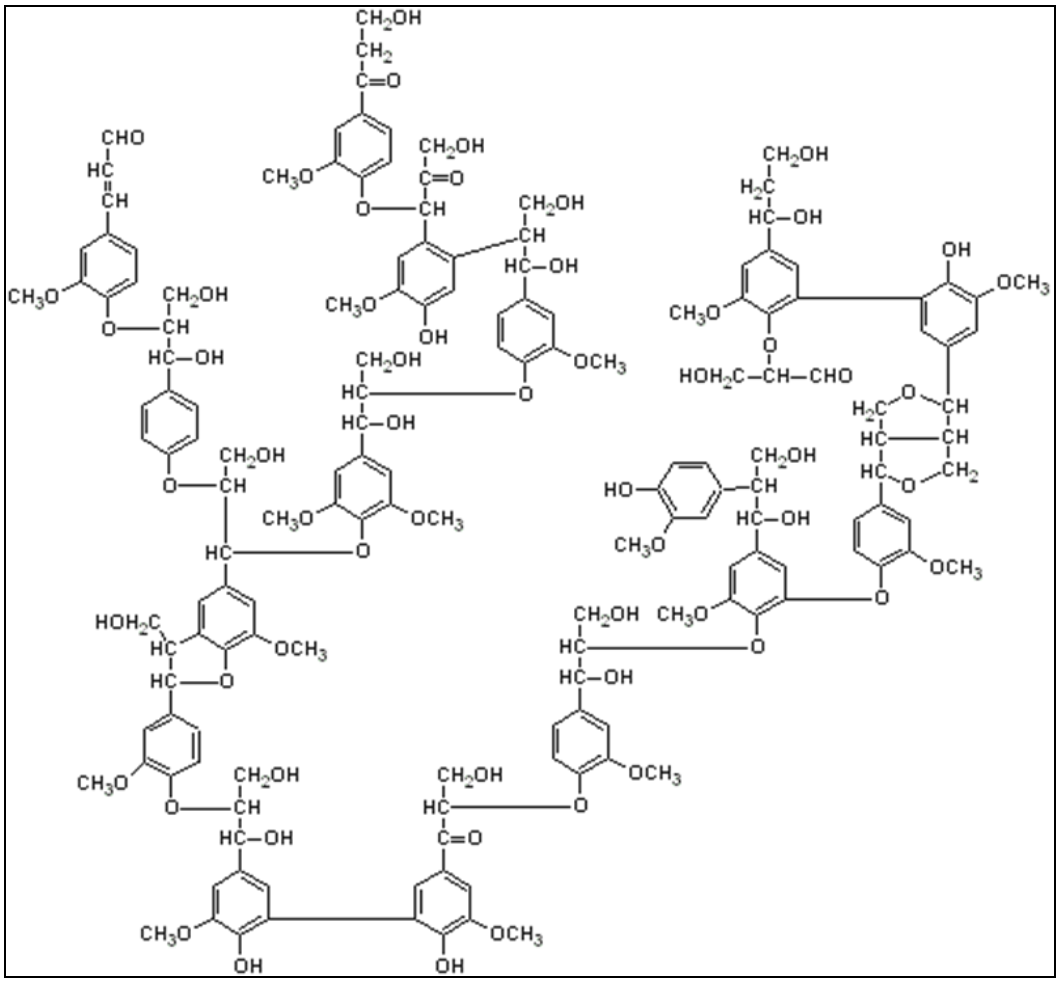
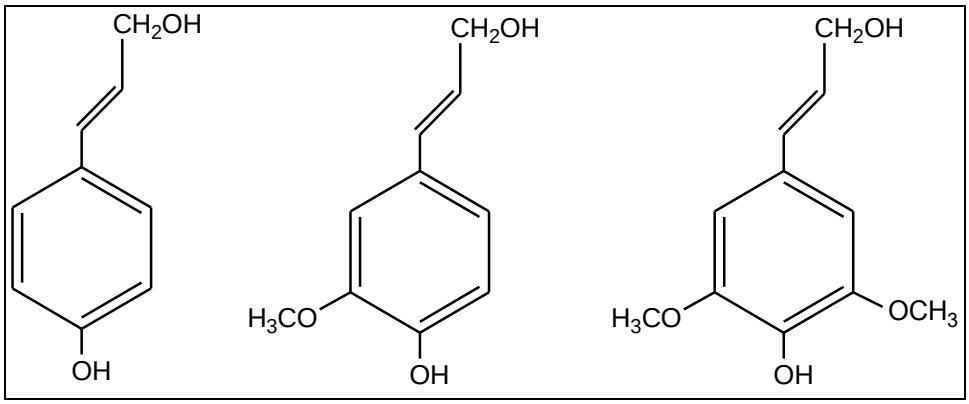


Figure 1.3: An example of chemical structure of lignin (Adler, 1977)



(a) **(b)** **(c)**

Figure 1.4**:** Three main phenylpropanoid units of lignin: (a) trans-*p*-coumaryl alcohol, (b) trans-coniferyl alcohol and (c) trans-sinapyl alcohol

The bio-structure of lignin is made of the free radical reaction of these monomers to form a stiff, three-dimensional cross-linked matrix (very similar to thermosetting resins such as phenol-formaldehyde resins). The lignin structure is characterized by rigidity to exterior physicomechanical acts, leading to shear stress and deformation. Therefore, these structures need a high flexibility towards the rearrangement of bonds within the lignin network, which leads to more condensed polymers. Chemically, lignin is considered a complex insoluble biopolymers, although many studies have been conducted, its chemistry and molecular biology is still not completely understood (Boerjan et al., 2003).

The lignocellulose complex contains four basic types of bonds: the carbon-to-carbon bonds, ether bonds, ester bonds, and hydrogen bonds. These bonds are responsible for providing linkages between the individual components of lignocellulose (intrapolymer linkages) and link the different components to form the complex (interpolymer linkages). The bonding positions are summarized in Table 1.1 (Faulon et al., 1994).

Table 1.1: Linkages between the monomer units that form the individual polymers lignin, cellulose and hemicellulose, and between the polymers to form lignocellulose (Faulon et al., 1994)

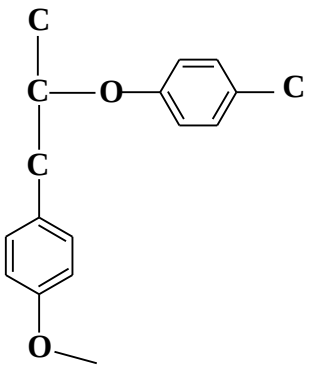
Bonds within different components (intrapolymer linkages)	
Ether bond	Lignin, (hemi)cellulose
Carbon to carbon	Lignin
Hydrogen bond	Cellulose
Ester bond	Hemicellulose
Bonds connecting different components (interpolymer linkages)	
Ether bond	Cellulose-Lignin Hemicellulose
Ester bond	Hemicellulose-lignin
Hydrogen bond	Cellulose-hemicellulose Hemicellulose-Lignin Cellulose-Lignin

The main kinds of linkages that connect the monomers within the lignin polymer are carbon-to-carbon bonds and ether bonds (Table 1.1). The total fraction of ether linkages in the lignin molecules accounted for approximately 70% of the total linkages between monomer units. The remaining 30% of the total bonds between the units represent the carbon-to-carbon linkages (Henriksson, 2007). The most common types of linkages which are found in the lignin structure illustrated in Figure 1.5 (Dence and Lin, 1992; Sjöström, 1993). In addition to the predominant linkages, at least 20 different linkage types have been identified (Whetten et al., 1998).

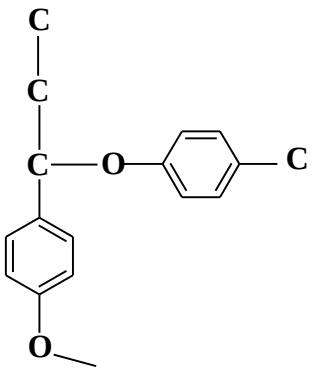
A wide range of functional groups are characterized in lignin. These groups are capable of meeting industrial requirements. The effectiveness of lignin mainly depends on the aliphatic and phenolic hydroxyl groups, as well as the carboxyl groups. These groups vary with the source of lignin and the extraction process used to obtain lignin. The solubility of lignin depends largely on the percentage of these functional groups. Generally, most types of lignin are quite soluble in alkaline solutions as a result of the ionization of carboxyl and hydroxyl functional groups

(Henriksson, 2007). In the aromatic rings on lignin, only about 10–13% of the phenolic hydroxyl groups are free to form neighboring phenylpropane linkages, whereas the others form ether linkages (Henriksson, 2007). The phenols content is important because it has a major role in chemical reactions, especially in modified lignin because it is the most reactive site in lignin structure.

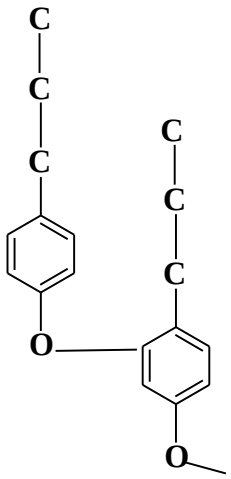
Ether linkage



β-O-4



α- O-4



4-O-5

Carbon - Carbon Linkages

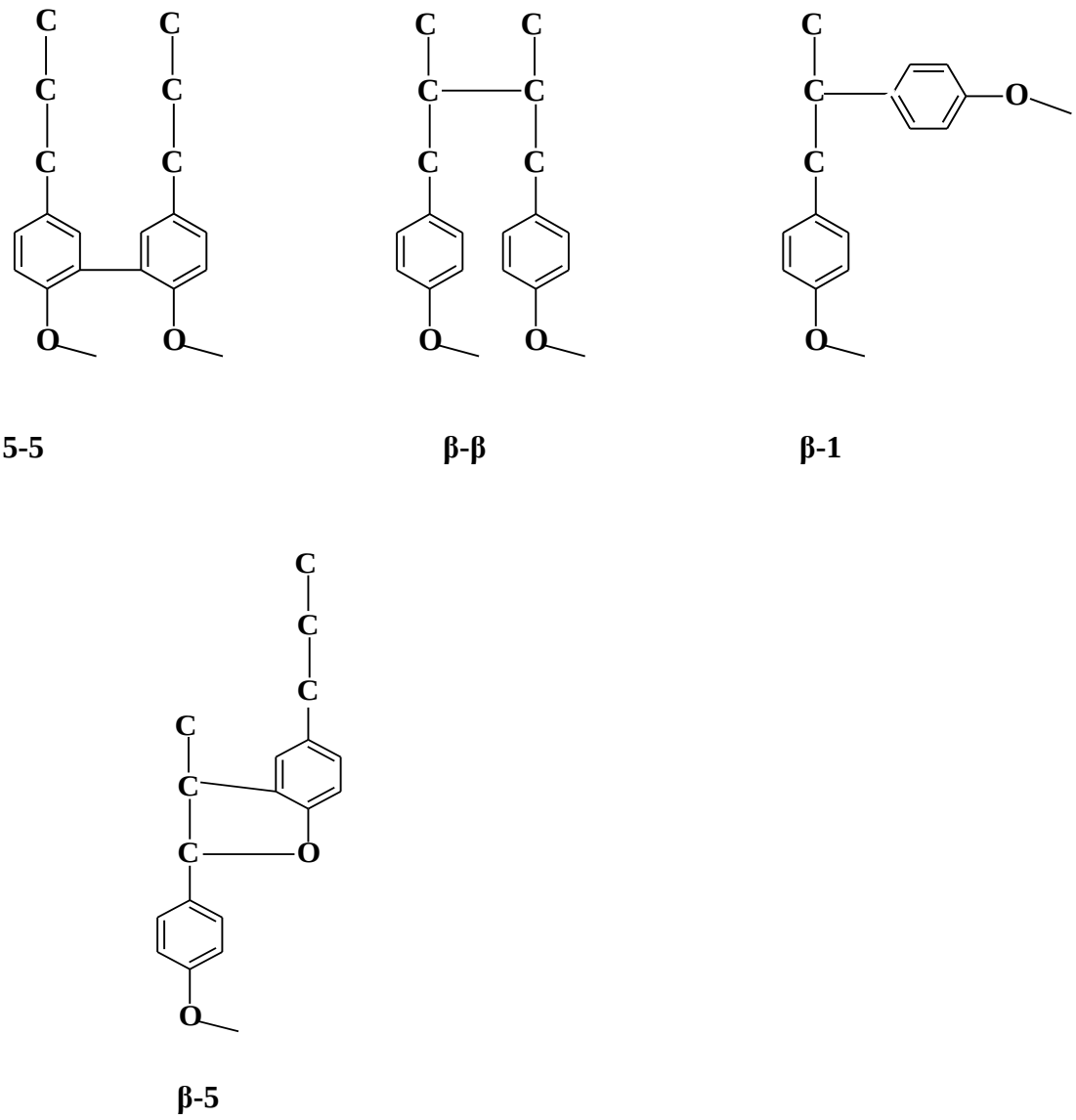


Figure 1.5: Common intermonomeric linkages in a lignin molecule (Henriksson, 2007)

Lignins are separated from the other parts of the lignocellulosic complex by physical and/or chemical means; these materials can be obtained as by-products of various processes, such as bioethanol production and papermaking. The botanical source affects lignin properties, but the delignification (pulping) process and the extraction procedures significantly affect the lignin structure, purity, and other characteristics (Lora et al., 2008; Lora and Glasser, 2002). Generally, chemical pulping is a way to remove lignin from wood (delignification) by altering the

chemical composition to produce soluble fragments of the polymer. Several different processes are used to produce chemical pulp, but the Kraft pulping process is considered the most common worldwide. To develop a modern paper manufacturing process, the use of the alkaline pulping process with wood as raw material was patented by Hugh and Burgess in 1854 because wood is readily available and fairly inexpensive. In the Kraft pulping process, lignin removal is done by treating wood chips with sodium sulfide under alkaline conditions at elevated temperatures. Kraft delignification occurs by modifying the lignin structure in two different ways. First, the lignin structure is degraded into smaller units by cleaving the linkages of inter-units. Second, the lignin structure is made more soluble in the cooking liquor via the introduction of hydrophilic groups in polymer and cleaved fragments (Gierer, 1980). These phenomena occur when the linkages between phenylpropane units are cleaved to generate free phenolic hydroxyl groups. The existence of these hydroxyl groups increases the hydrophilicity of lignin and lignin fragments; thus, the lignin solubility is increased in the cooking liquor. Meanwhile, the carbon-carbon linkages become more stable and tend to survive in the Kraft pulping process (Sjöström, 1993). During cooking, most of the β-O-4 linkages in lignin structures are hydrolyzed (>95%) and lignin is degraded into fragments of different molecular weights that are soluble in the alkali solution (Gellerstedt and Zhang, 2001). The color of spent liquor from cooking is deep brown because of the lignin fragments. At this point of the process, hemicellulose is still attached to lignin. Figure 1.6 shows the three distinct phases of the dissolution of lignin and hemicellulose.

The initial delignification step occurs at temperatures less than 150 °C; approximately 20% of lignin and carbohydrates are dissolved during this step. Thereafter, at above 150 °C in the bulk phase, approximately 90% of lignin has been

selectively dissolved, without dissolving more carbohydrates. The final delignification step includes final treatment at 170 °C, which would entail the removal of the remaining lignin with a significant loss of carbohydrates (Gellerstedt and Lindfors, 1984). This step can practically stop the cooking procedure of the bulk phase because continuing to the final phase could lead to a loss of quality and low yield. Therefore, the cooking time should be adjusted to achieve the target quality.

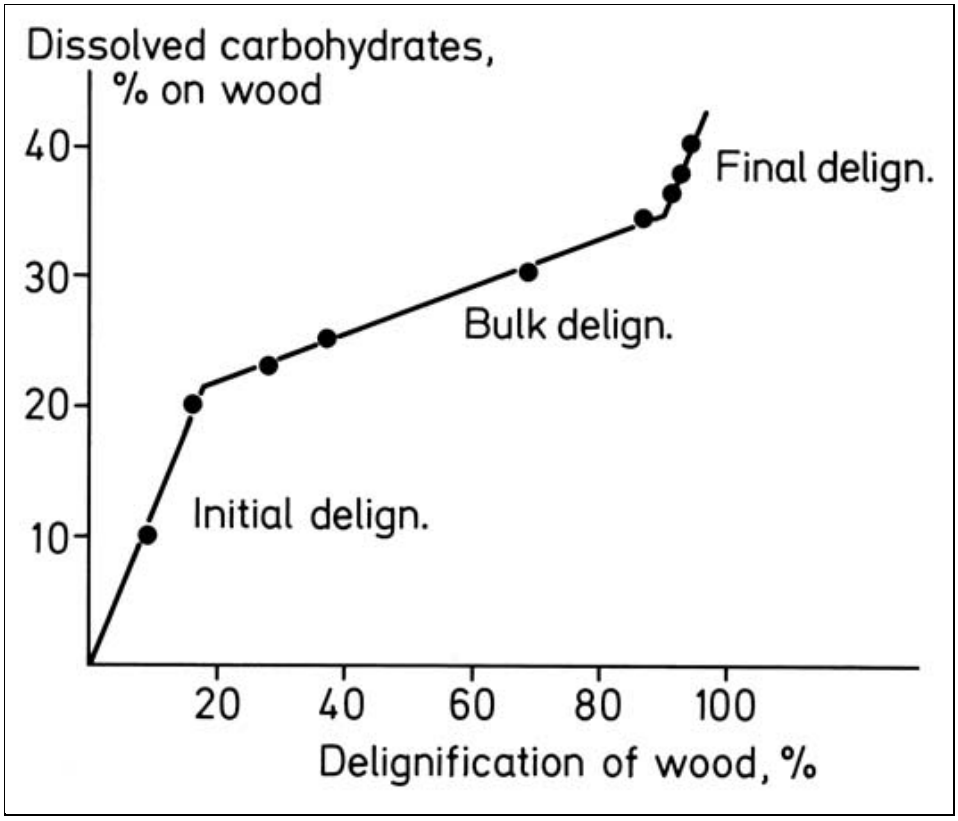


Figure 1.6**:** The dissolution of lignin and hemicelluloses during Kraft pulping that proceeds in three distinct phases (Gellerstedt and Lindfors, 1984)

The delignification process used for the isolation of lignin has an important role in defining the features of the final structure. To dissolve lignin, nucleophiles, such as hydroxide ions and hydrogen sulfide, are introduced. The cleavage of ether bonds would increase the amount of free phenolic groups.

Kraft lignin has many applications, although most are still in the pilot scale. Products based on Kraft lignin include carbon fibers (Kadla et al., 2002), carriers for pesticides and fertilizers (Zhang, 2008), binders, resins (Tejado et al., 2007), blending materials containing thermoplastic polymers (Gosselink et al., 2005), and ion exchange resins (Zoumpoulakis and Simitzis, 2001).

Organosolv fractionation is one of the promising pretreatment technologies, wherein lignin production relies on the use of systems based on various organic solvents. Moreover, this method has become a subject of much scientific research activities, which generated increasing interest in the paper and pulp industry after the trend to reduce the environmental impact of these materials (Zhao et al., 2009). In the organosolv process, lignocellulosic feedstock is treated with an organic solvent, such as alcohols and organic acids, with the presence of water as a co-solvent to reduce the vapor pressure and lower the pH thereby solubilizing hemicellulose for the extraction of lignin from lignocellulosic biomass. Additionally, the use of organic solvents limits the formation of sulfated byproducts. Compared with other pulping processes, one of the main benefits of organosolv pulping is the highly effective delignification of lignocellulosic feedstock prior to enzymatic hydrolysis, whereas the chemical structure of lignin has been largely preserved and less condensed than other pretreated lignins. In addition to delignification, hemicellulose dissolves in the organic solvent and, thus, improves the enzymatic digestibility of the cellulose fragments to fermentable sugars (Zhao et al., 2009). Another advantage of the organosolv process is the higher purity of retrieved lignin and the absence of sulfonates, which makes it more environment friendly (Pan et al., 2006, 2005; Zhang, 2008).

The organosolv pulping process uses various organic solvents such as aliphatic alcohols (Pan et al., 2006; Solár et al., 2001), diols (Jiménez et al., 2004), organic acids (Ibrahim and Glasser, 1999), and amines (Heitz et al., 1994).

However, the most common organosolv processes are the ethanol organosolv (Alcell) and acetic acid pulping processes. Both contain mineral acids in small amounts, such as sulfuric acid or hydrochloric acid (Acetosolv). Generally, alcohols with low molecular weights are most commonly used in organosolv pulping; in addition, primary alcohols are better agents than secondary or tertiary alcohols for delignification (Zhao et al., 2009). Among the alcohols, the ethanol solvent is the most widely used in organosolv pulping. Given its low toxicity, ease of recovery, and low cost, ethanol is the most preferred alcohol. The Alcell® Process technology was developed in 1990 for industrial scale production in Canada (El Hage, 2012). Organosolv lignin can be used to produce certain valuable products and green materials, such as adhesives (Çetin and Özmen, 2002a), films, fibers (Pereira et al., 2007) and biodegradable polymers (El Hage et al., 2009).

1.4 Tannin

Tannins are polyphenols that exist naturally and are widely distributed in plants. These compounds are water-soluble phenolics with molecular weights ranging from 500 to 3000. In addition, tannins have the capacity to bind with precipitate alkaloids, gelatin, and other proteins (Karamać et al., 2007). Natural tannins are divided into two main classes (Fig. 1.7). The condensed polyflavonoid tannins (proanthocyanidins) are biopolymers based on flavan-3-ol, which would liberate catechins and anthocyanidins as end groups in alcohol solution and at

elevated temperatures. Meanwhile, gallotannins and ellagitannins belong to the group of hydrolyzable tannins. Gallotaninns consist of galloyl esters of glucose or quinic acid, whereas ellagitannins are derivatives of hexahydroxydiphenic acid (Hagerman et al., 2005). Chemically and commercially, condensed tannins from natural polymers are more interesting in the production of adhesives and resins. These tannins account for more than 90% of the total world production of chemicals. To precipitate proteins, to reduce the use of vitamins and minerals, and to inhibit digestive enzymes, tannin can be considered an antinutrient compound of plant origin. Several studies have mentioned the antiradical and antioxidant activity of tannins (Alasalvar et al., 2006; Amarowicz, 2007; Amarowicz et al., 2004). Treatment of leathers with natural vegetable tannins in the leather tanning industry provide some advantages, such as more resistant to mechanical ware and less susceptible to biological and other types of attack.

Tannin application in corrosion studies has been investigated by many researches. Mangrove tannin that was extracted from the mangrove bark was used as anticorrosion inhibitors. It has been found that the mangrove tannin effectively inhibits the corrosion on copper metal in hydrochloric acid solution. The results of the electrochemical and weight loss methods showed that the inhibition efficiency of mangrove tannin increases with increased concentrations (Shah et al., 2011). The influence of halide salts viz., KCl, KBr and KI on the corrosion inhibition of mangrove tannin were also investigated. Results show that mangrove tannin alone provided satisfactory inhibition on the corrosion of mild steel and it was also found that the inhibition efficiency increased synergistically in the presence of halide ions (Ridhwan et al., 2012). The synergy between iodide ions and mangrove tannin extracted from mangrove bark (waste products of the charcoal industry) was tested

on the inhibition of corrosion of mild steel in 0.5 M HCl and 0.25 M H_2SO_4. It was compared with the inhibition provided by mimosa and chestnut tannins. Mangrove tannins showed comparable inhibitive properties to those of commercial mimosa and chestnut tannin (Ridhwan et al., 2015).

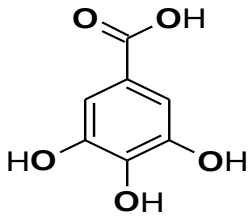
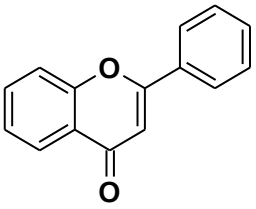
Basic Unit	 Gallic acid	 Flavone
Class/Polymer	Hydrolyzable Tannin	Condensed Tannin

Figure 1.7: Structure of tannin

1.5 Biomass liquefaction

Biomass can be converted into liquid or gaseous products, which can be used in organic synthesis or engines of internal combustion (Pan et al., 2009). Generally, the main routes for the production of biofuels and various chemicals from biomass are based on biochemical and thermochemical conversions (Demirbas, 2001).

Thermochemical conversions involve three main processes, namely, gasification, pyrolysis, and liquefaction. Gasification uses heat at temperatures higher than 1000 °C to convert lignocellulosic biomass into synthetic gas with a mixture of CO, H_2, and CH_4, in addition to CO_2 and N_2 (Demirbas, 2001). Pyrolysis involves the thermal decomposition of lignocellulosic biomass by heat in the absence

of O_2 to obtain charcoal (solid), bio-oil (liquid), and fuel gas (Demirbas & Arin, 2002). Thermochemical processes involve two types of liquefaction. The first type is comparable to pyrolysis and called direct liquefaction. However, liquefaction occurs at temperatures between 250 and 350 °C in the absence of O_2 and is usually conducted under pressures of approximately 5–10 MPa (Demirbas, 2000), whereas pyrolysis is conducted at temperatures between 380 °C and 550 °C. The second type of liquefaction process dissolves lignocellulosic biomass in organic solvents with or without a catalyst at moderate temperatures (100–250 °C). Given its simple preparation, high level of production, high energy conversion, and high capacity of organic material treatment, the liquefaction process has attracted more attention (Ye et al. 2014).

Much work has been done on the liquefaction process of biomass in relation to the raw materials, solvents, and catalysts. Raw materials include algae (Chow et al., 2013; Duan et al., 2013), crop residue (Liu et al., 2013; Zhang et al., 2012), and wood (Cheng et al., 2010; Rivas et al., 2013; Tekin and Karagoz, 2013).

Other studies (D'Souza and Yan, 2013; Zou et al., 2009) have reported that a series of reactions mainly occurred during the liquefaction process, including decomposition, esterification, and polycondensation. The liquefied wood contains depolymerized products from the β1–4 glucosidic bond cleavage of the cellulose and hemicelluloses molecules as well as from low molar mass oligomers. The complex structure of the lignin molecule can be broken into smaller fragments. However, the associated reaction pathways and products have yet to be defined completely.

The liquefaction of wood and other lignocellulosic materials with organic solvents, such as phenols and polyhydric alcohols, is a unique thermochemical conversion process among the biomass applications because this process combines

the useful, functional groups of the biomass and organic solvent to obtain a large variety of biopolymers (Pan, 2011). This process has been studied extensively by several groups. These biopolymer products include coatings (Budija et al., 2009), carbon fibers (Xiaojun and Guangjie, 2010), foams (Alma and Shiraishi, 1998), and adhesives (Alma and Bastürk, 2001; Fu et al., 2006; Kobayashi et al., 2000). The liquefied wood can be used as part of the adhesive mixture because of the presence of free hydroxyl groups, which can polymerize with different functional groups to produce various polymers or to self-crosslink (Budija et al., 2009). The liquefied wood adhesives can also be combined with a mixture of synthetic adhesives or with other natural materials, such as tannins (Cuk et al., 2011).

Lignin has also been used for the production of polyol compounds through the liquefaction process, which can be employed in the preparation of various types of resins.

1.6 Additives

The introduction of a second component to polymers has been accepted; this component is often used to modify the characteristics of the products and to acquire new polymer materials with improved properties. Composite materials have a pivotal role in industries that are now considered the most progressive worldwide. Generally, the term “composite” is given to materials made of more than one component. Polymer composites are a mixture of polymers with inorganic or organic additives that have certain geometric forms (spheres, flakes, fibers, and particulates). A wide range of polymer characteristics can be improved by composite technologies, such as their mechanical, thermal, durability, chemical stability, barrier, flame retardance,

corrosion resistance, biodegradability, magnetic, optical, and electrical properties (Armentano et al., 2010; Cosoli et al., 2008; Ma et al., 2006; Pandey et al., 2005).

Fillers are substances that can be added to various polymer systems to reduce the cost or improve their properties (Giannelis, 1998; Pavlidou and Papaspyrides, 2008). This material can be added as a solid, liquid, or gas. For example, the use of a minimal percentage of clay loading can lead to significant improvements in the mechanical and thermal properties (Giannelis, 1998; Pavlidou and Papaspyrides, 2008). In general, the fillers used to modify the properties of polymers can be classified into two categories: inert fillers and active fillers. Inert fillers come from inorganic mineral powders, such as kaolin, diammonium phosphate, porcelain clay (which is frequently used), sodium silicate, and magnesium oxide. These fillers are used to reduce cost**.** These mostly hydrophilic materials can be dispersed in adhesives. Active fillers are organic compounds, which swell when dissolved in a solution. These fillers include the cellulose-type fillers (wood powder, bark powder, etc.), protein-type fillers (soy protein, blood powder, etc.), and starch-type fillers (wheat flour, etc.). These materials have the ability to react with resins.

Clays are one group of additives that have been widely used in the preparation of polymeric composite materials. Recently, increasing attention has been given to the development of polymer/clay nanocomposites because of their dramatically improved properties as compared with conventional fillers after the addition of very low portions of the filler (Thostenson et al., 2005). Clay minerals are used in soil science and sedimentology to refer to particles formed by the combination of tetrahedral and octahedral aluminosilicate ($[SiO_4]^{-4}$ and $[AlO_4]^{-5}$) layers that are 1 nm thick with 200–300 nm lateral dimensions, as shown in Figure

1.8 (Alexandre and Dubois, 2000). Clay minerals are important materials that are mainly hydrated aluminosilicates with neutral or negative charges (Murray, 2000). The internal and external cations can be changed by inorganic or organic cations (Alexandre and Dubois, 2000; Lebaron et al., 1999).

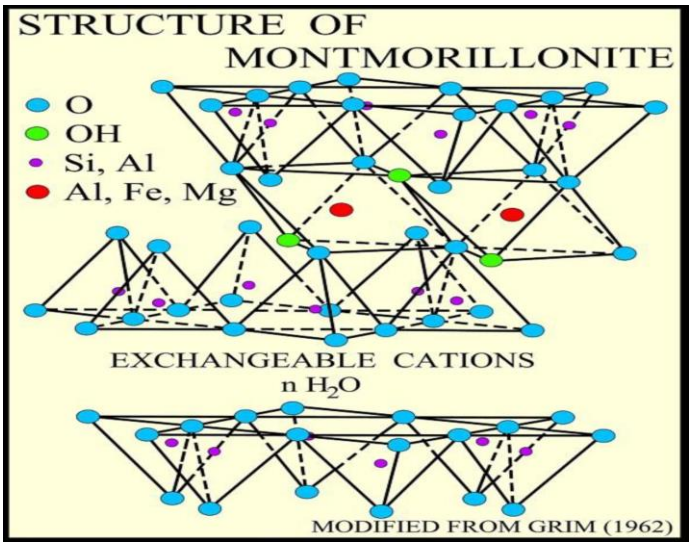


Figure 1.8: Montmorillonite structure (Sansuri 2010)

The hydrophilic nature of clays makes them poorly suited for mixing with most hydrophobic polymer materials. In addition, the poor physical interaction between the organic components in polymeric materials and the inorganic components in clay leads to their separation and the formation of discrete phases. Therefore their mixtures have poor properties, and this incompatibility prevents the dispersion of clay layers within polymer matrix, thereby leading to weak interfacial interactions (Giannelis, 1996; Singla et al., 2012; Van Olphen, 1977). Moreover, electrostatic forces tightly link the clay platelets with each other. Only some hydrophilic polymers are miscible with layers of clay; these materials are used in the preparation of polymer–clay composites such as poly(vinyl alcohol) and poly(ethylene oxide) (Pavlidou & Papaspyrides 2008).

For these reasons, clay requires pretreatment before it is used as filler in polymer composites. These piles of clay platelets have dimensions much larger than one nanometer. Therefore, untreated clay would be ineffective during use because most of the clay would be trapped inside and unable to react with the polymer matrix. Generally, the intercalation of clay with different organic species is the basic condition for compatible composite materials to ensure the interaction between the clay surfaces and the polymeric components. The intercalation or surface modifications decrease the surface energy of clay layers and match their surface polarity with polymer polarity. The low surface energy of organoclays is more compatible with organic polymers and can intercalate with the interlayer space under specific experimental conditions.

This spacing of organoclays is affected by a variety of factors, including the chemical structure of the surfactant, the degree of cation exchange, and the silicate layer thickness (Maiti et al., 2002). Organically modified clays have been extensively studied in various practical applications in the field of organic-inorganic hybrids, composites, and nanoscale composites (Singla et al., 2012). The surface modification of clay layers can be performed through an ion exchange process via the replacement of cations, such as sodium and calcium, in the interlayer space by ammonium or phosphonium surfactants, which usually include benzyl groups and short aliphatic chains (Ahmad et al., 2009). In addition to modifying the surface and increasing the hydrophobicity of clay layers, the introduction of alkylphosphonium ($R_4P^+X^-$) and alkylammonium ($R_4N^+X^-$) cations into the clay layers increases the distances and spacing of the clay layers, which facilitates the intercalation of the polymer chain during the preparation of nanocomposites (Chigwada et al., 2006). Moreover, the

cations ($R_4N+ X^-$) and (R_4P+X^-) can provide the necessary functional groups that have the ability to interact with the polymer chains or to initiate polymerization processes, thereby increasing the interfacial interactions, as shown in Figure 1.9.

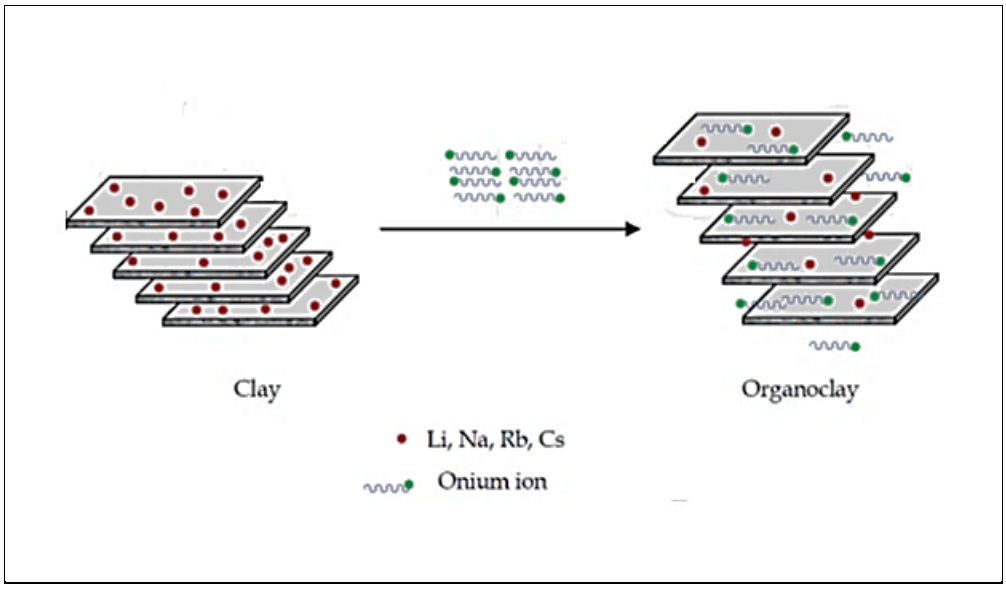


Figure 1.9: Scheme of the modification of clay layers by organic onium cations (Olad, 2011)

1.7 Problem statement

Wood adhesives have a very important role in the industry of wood-based panels. The performance of wood panels eventually depends on the significant efficiency of the adhesive. Synthetic condensation resins based on formaldehyde have been widely used; these resins include urea formaldehyde (UF), phenol formaldehyde (PF), resorcinol formaldehyde (RF), and melamine formaldehyde (MF). The source of all the components of these adhesives is derived from fossil oil. The PF resin is drastically used as a wood adhesive and is also used in boards for use under exterior weather conditions, such as weatherproof plywood, oriented strand

boards (OSB), medium density fiber boards (MDF), or particle boards. The phenol and formaldehyde used to prepare PF resin are toxic materials and contribute to CO_2 emissions, thereby influencing climate changes. Both materials are non-renewable and toxic. In addition, the World Health Organization's International Agency for Research on Cancer (IARC; an advisory board to the World Health Organization) in 2004 reclassified formaldehyde from group 2A (probably carcinogenic to humans) to group l (carcinogenic to humans). This reclassification was primarily based on the results of a National Cancer Institute (NCI) study of workers with occupational exposure to formaldehyde. These results indicated that formaldehyde causes nasopharyngeal cancer (NPC) and is associated with leukemia. However, an outright ban on the use of formaldehyde in wood-based products is currently unlikely because the industry is dependent on the current efficient technologies.

Certainly, formaldehyde is evidently liberated during the production and use of composites of wood bonded with formaldehyde-based adhesives. This formaldehyde emission primarily comes from the remaining free formaldehyde in the adhesives as well as the hydrolysis of adhesives.

Malaysia has more than 4 million hectares of oil palm plantations that yield an estimated amount of 90 million tons of renewable biomass (front, trunk, palm press fiber, shell, and empty fruit bunches), which is generated from the mechanical processes of palm oil production (Malaysia Palm Oil Board, 2013). Unfortunately, oil palm biomass is still treated as a waste without considering the value of their components, such as cellulose, hemicelluloses, and lignin (Mohamad Ibrahim et al., 2006). The biomass remnants must be eliminated in a systematic and scientific manner because the presence of such residues is a danger to the environment.